Obtaining and Interpreting Near-Infrared Wavelength Modulation Absorption Signals from Hot Fire Gases: Practical Issues

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Introduction and Background

Near-infrared tunable diode laser absorption spectroscopy (TDLAS) shows promise for measuring concentrations of several gaseous species important in fires, including CH_4, O_2, C_2H_2, C_2H_4, CO, CO_2, and H_2O [1]. Researchers at NIST are presently studying the possible application of near-infrared TDLAS for rapid measurement of CO concentration in and around fires. Near-infrared diodes are compact, spectrally narrow, and rapidly tunable, and the potential exists to deliver diode light into and out of real-scale fires using rugged and readily-available silica fiber optics. The goal of the NIST project is to develop a diode laser sensor capable of measuring CO concentration at temperatures between 300 K and 1200 K in fire gases partially obscured by soot. This abstract describes some practical signal interpretation issues found to be important during sensor development.

Previous studies on the use of near-infrared diodes for CO measurement have focused on determining CO amounts in room-temperature absorption cells with controlled gas composition [2-5]. Some recent studies of CO in combustion gases employed rapid probe sampling with a multi-pass cell/diode laser arrangement [6], and an in situ measurement of CO concentration in the hot exhaust of a premixed methane/air flame was recently reported [7]. Near-infrared TDLAS has been used in fire research to quantify hydrogen fluoride concentration in post-flame gases following fire suppression [8].

Experiments and Modeling[1]

The amount of light absorbed by a molecule is quantified using the Lambert-Beer law, $\tau_{\tilde{\nu}} = \exp\left[-S(T)g(\tilde{\nu}-\tilde{\nu}_0)NL\right] = \exp\left[-\alpha(\tilde{\nu})\right]$, where $\tilde{\nu}_0$ is the transition center wave number (cm^{-1}), $\tau_{\tilde{\nu}}$ is the fractional transmittance at $\tilde{\nu}$, T is the gas temperature (K), S(T) is the T-dependent line strength (cm^{-1}/molecule$\cdot cm^{-2}$), $g(\tilde{\nu}-\tilde{\nu}_0)$ is the line shape function normalized to unit area (cm), N is the absorber number density (molecule/cm^3), L is the path length (cm), and $\alpha(\tilde{\nu})$ is the absorbance. A Voigt profile, accounting for collisional (Lorentzian) and thermal (Doppler) broadening, is sufficient for computing $g(\tilde{\nu}-\tilde{\nu}_0)$ in most combustion work [1]. Wavelength modulation spectroscopy (WMS, [9]) is the sensitive detection scheme examined here. WMS signals resemble derivatives of the transmittance profile, and are modeled using Equations 1 through 6 of Ref. [10] for the present work.

The CO second overtone R(23) transition centered at 6410.9 cm^{-1} (near 1.56 μm) is targeted for this study. The T-dependent line strength for this transition taken from the HITEMP database [11] is $S = 8.78 \times 10^{-25}$ cm^{-1}/molecule$\cdot cm^{-2}$ at T = 300 K and $S = 9.14 \times 10^{-24}$ cm^{-1}/molecule$\cdot cm^{-2}$ at T = 1200 K. The air-broadened and self-broadened half-widths at half maximum (HWHM) at 296 K are 0.045 cm^{-1}/atm and 0.051 cm^{-1}/atm, respectively, with a T-dependence coefficient of 0.69. Assuming a minimum detectable absorbance of $\alpha(\tilde{\nu}_0) = 1\times10^{-5}$, the Lambert-Beer law predicts that a concentration of 0.7 % by volume of CO can be detected in a 10 cm path at 300 K, while 0.1 % can be detected at 1200 K. Concentrations of CO as high as 5 % by volume exist in the exhaust of underventilated enclosure fires [12]. Hence, the R(23) line should be sensitive enough to detect CO concentrations of interest in fire research.

The present diode laser is a fiber-coupled InGaAsP distributed-feedback laser packaged by Alcatel. The laser beam is delivered to the measurement location by a 10 m long, 9 μm diameter single-mode fiber and is collimated to

[1] To describe experimental procedures, it is occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular products or equipment are necessarily the best available for that purpose.

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a diameter of 0.5 mm using a gradient-index lens. The collimated beam is aimed across the optical path and focused by a convex mirror onto an InGaAs photodiode. For this study, either a room-T absorption cell or a flame are placed in the optical path. A laser diode controller is used to vary the laser wave number by changing either the laser temperature (coarse tuning) or the injection current (fine tuning). The laser is operated with a temperature of 51.4 °C and a nominal current of 50 mA. The steady-state DC laser tuning rate for 51.4 °C is 0.0245 cm^{-1}/mA.

Software developed by Southwest Sciences, Inc. for data acquisition and control was used on a personal computer to perform the present experiments [13]. A 39 Hz voltage ramp ranging from -0.4 V to +0.4 V was generated electronically and applied to the laser injection current via the diode controller. Combining these voltages with the controller transfer function (20 mA/V), the current ramp ranged between -8 mA and +8 mA. The ramp was generated in 256 bins at a rate of 100 μs per bin. A hyperbolic-tangent waveform with duration of 50 % of the sweep time was applied between sweeps to minimize electronic ringing. A modulating sine wave with a frequency of either 49 kHz (for 2f) or 24 kHz (for 4f) was superimposed on the slow ramp. The sine wave amplitude was either 0.4 V (8 mA) or 0.5 V (10 mA) for the experiments described here. The ramp and sine amplitudes cannot be converted directly from current to wave number using the DC laser tuning rate because of laser response-time effects. A digital lock-in amplifier (300 μs time constant) demodulated the transmitted signal at either twice or four times the modulation frequency. This high frequency detection scheme reduces laser excess noise (proportional to 1/f), allowing sensitive detection [9]. The lock-in output signal was normalized by the detector DC signal before processing, and 250 sweeps were averaged for each spectrum.

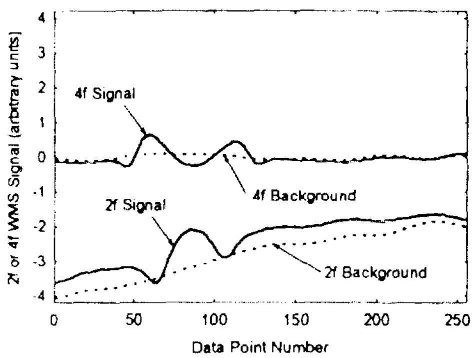

Fig. 1. 2f and 4f signals and backgrounds for CO in a 13-cm cell with P = 19.5 torr and T = 300 K.

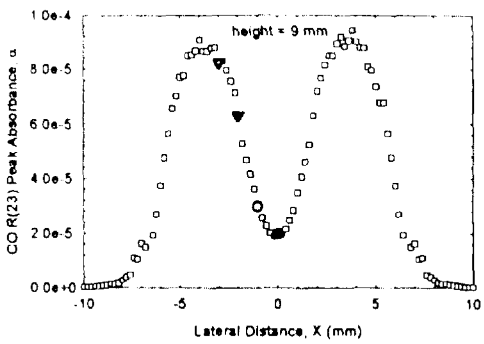

Fig. 2. Lateral profile of CO R(23) peak absorbance in the NIST Wolfhard-Parker burner at a height of 9 mm from the burner. Calculated from previous CO concentration and T measurements.

Sloping baselines caused by laser amplitude modulation were subtracted from the signals. Figure 1 shows 2f and 4f signals collected in a 13-cm absorption cell filled with low-pressure, pure CO, along with background signals collected in the absence of the cell. The 2f background has a strong non-zero slope caused by amplitude modulation, but the 4f background is relatively flat. Additionally, the 4f signal is slightly weaker than the 2f signal. The baseline slope limits the 2f measurement sensitivity by consuming the lock-in amplifier dynamic range. These trends agree with previous work concerning the behavior of diode-laser amplitude modulation at higher harmonics [9]. Because of the 2f backgrounds, more sensitive measurements can be made with 4f WMS in spite of the lower signal levels. Hence, 4f is used for the present study.

A Wolfhard-Parker (WHP) slot burner is used to achieve known CO mole fraction (χ_{CO}) and T combinations along a uniform, 4.1 cm path. The WHP flame has been studied extensively by Smyth and coworkers, and a comprehensive database is available [14]. T and χ_{CO} were measured previously with radiation-corrected thermocouples and mid-infrared TDLAS, respectively [15]. The burner operating condition used here is identical to that used previously. Figure 2 shows an expected lateral profile of peak CO absorbance calculated using the Lambert-Beer law. Table I provides information about the four data points from the profile used for sensor development.

Table I. Four WHP Data Points with T < 1200 K

Symbol	X (mm)	χ_{CO}	T (K)	$\alpha(\tilde{\nu}_0)$
closed circle	0	0.0075	550	2.0×10^{-5}
open circle	- 1	0.0094	660	3.0×10^{-5}
closed triangle	- 2	0.018	880	6.3×10^{-5}
open triangle	- 3	0.026	1170	8.2×10^{-5}

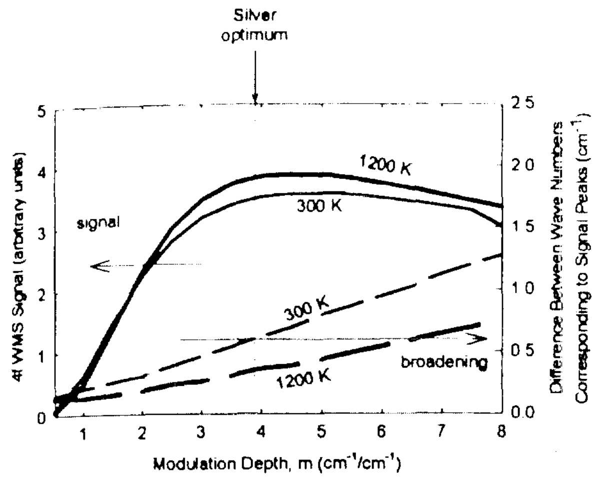

Fig. 3. Calculated effect of m on CO R(23) 4f signal and broadening for two temperatures.

Results: Modulation Depth Effects

WMS is characterized by the modulation depth, m, defined as the ratio of the modulating sine wave amplitude (cm^{-1}) to the HWHM of the spectral line (cm^{-1}). Reid and Labrie showed that 2f WMS signals are maximized when m = 2.2 [16]. Silver extended their analysis to higher harmonics and showed that m = 3.9 is optimum for 4f WMS [9]. Figure 3 shows results of an analysis like the one performed by Silver to reveal the optimum. While Silver's calculations were for general Doppler- and Lorentz-broadened lines, the present analysis is specific to the R(23) CO line and is based on Voigt profiles. The 4f WMS signal (defined as the peak-to-central-valley signal difference) and the wave number spacing between signal peaks are depicted as a function of m for T = 300 K and T = 1200 K. For low values of m, the signal increases with m, reaching a maximum near m = 3.9 and staying constant or decreasing thereafter. Values of m > 3.9 result in excess broadening of the 4f spectrum; this broadening is undesirable because broad signals are more likely to overlap with interfering signals from other species or exceed the laser scan width.

While the idea of selecting one optimum modulation depth and keeping it constant is appealing, it may not be practical for fire research applications because T varies with time and spectral linewidths vary with T. Figure 4 shows the HWHM of the atmospheric-pressure Voigt profile for the R(23) line as a function of T. The HWHM steadily decreases as T increases. It would be impractical to maintain a constant value of m for all values of T, since the modulating sine wave amplitude would need to be adjusted before every scan. In practice, a single sine wave amplitude is initially selected (perhaps using a room-T absorption cell) and used throughout data collection. Figure 4 shows predictions of the way that m would vary with T if (1) the modulation amplitude were initially optimized (m = 3.9) with a 300 K cell, or (2) the modulation amplitude were initially set to achieve m = 2.0 with a 300 K cell. For cases (1) and (2), m increases to 7 and 3.5, respectively, when T reaches 1200 K. Case (1) demonstrates that selecting the optimum modulation setting for room T will lead to over-broadened lines at higher temperatures. While not shown in this paper, experimental flame signals collected with the system optimized for a 300 K line were very broad. Case (2) is more desirable for practical measurements in fire gases.

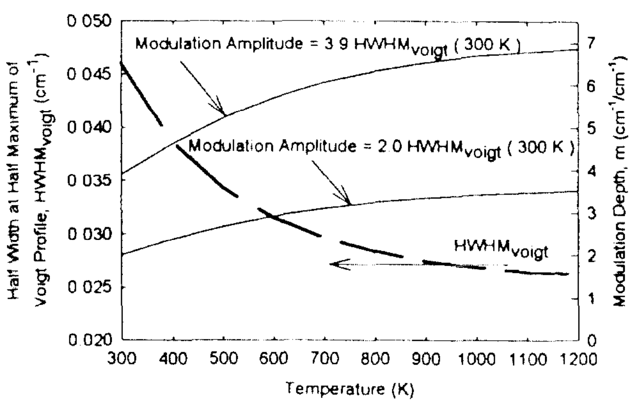

Fig. 4. Effect of T on CO R(23) HWHM and on m for different optimization methods.

Calibration is presently being explored as a method to quantify the measured signals. Calibration curves (graphs of 4f signal versus calculated peak absorbance) have been generated with known atmospheric-pressure mixtures of CO in air at T = 300 K and are shown on the left side of Fig. 5 for two modulation amplitudes. The calibrations are not expected to apply for T > 300 K because of lineshape variations. To check this hypothesis, WHP flame data are shown on the figure. (Refer to Fig. 2 for matching symbols). The high-T flame signals for the lower modulation amplitude (0.4 V or 8 mA) lie above the 300 K calibration curve. For the larger modulation amplitude (0.5 V or 10 mA), the flame signals lie closer to the 300 K calibration curve. The data trends can be understood by examining the right side of Fig. 5, which shows calibration curves generated by spectral modeling for cases (1) and (2) discussed earlier. The magnitudes of the curves are scaled so that the case (1) prediction matches the larger-modulation-amplitude experimental curve at its uppermost point. For case (1), the calibration curves for

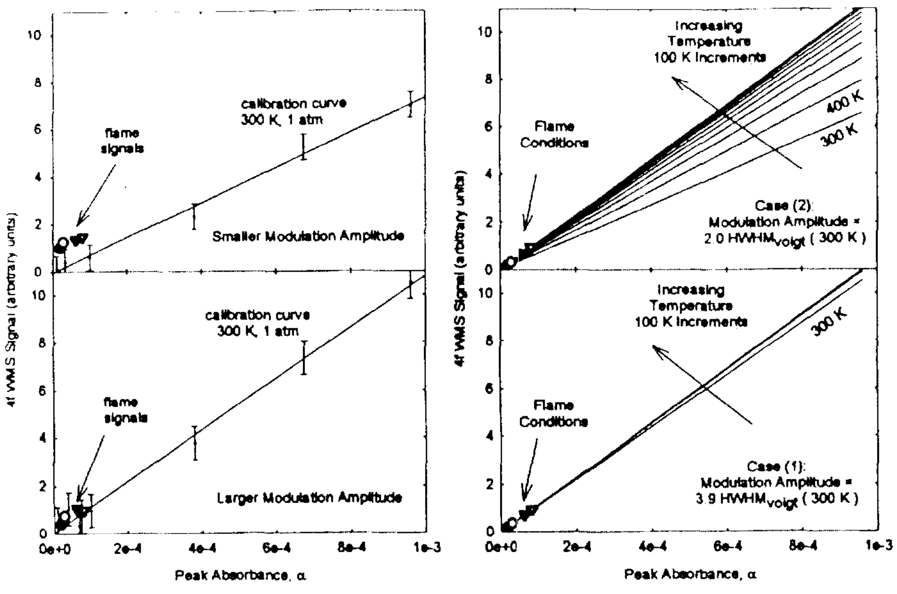

Fig. 5. Measured and calculated calibration curves and flame signals.

$T > 300$ K overlap, and the predicted flame signals fall on top of them, in agreement with the larger-modulation-amplitude experimental data behavior shown on the left half of the figure. For case (2), the calibration curves exhibit stronger T-dependence, in agreement with the experimental data shown on the left half of the figure. From these comparisons, it can be deduced that the larger-modulation-amplitude flame signals are over-modulated, while the smaller-modulation-amplitude flame signals are not. While the T-independence of the over-modulated calibration curves is desirable, the broadening caused by over-modulation is not.

Conclusions

For the present NIST laser system, 4f WMS is used rather than 2f WMS because 2f WMS sensitivity is limited by a strongly sloping background. Since m increases with T for the CO R(23) line, it should be set to a less-than-optimum value at room temperature to avoid over-broadening at higher temperatures.

Acknowledgments

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